THE CLAUSIUS INEQUALITY DOES NOT FOLLOW FROM THE SECOND LAW OF THERMODYNAMICS

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ABSTRACT. The example of macroscopic thermodynamical system violating the Clausius inequality is presented.

1. The gap in the proof of the Clausius inequality

The well-known Clausius inequality

$$\oint \frac{dQ}{T} \leq 0 \tag{1}$$

is supposed to be valid for any closed system undergoing a cycle. The more general formulation of this inequality

$$dS \geq \frac{dQ}{T} \tag{2}$$

is actually less clear because the definition of entropy for nonequilibrum systems is a subject of controversa. The rigirous version of (2) is the so-called Clausius-Duhem inequality

$$\int_A^B \frac{dQ}{T} \leq S_B - S_A, \tag{3}$$

where A and B are *equilibrum* states.

The proof of (1) may be found in any textbook on thermodynamics. Consider a system connected to a thermal energy reservour at a constant absolute temperature of T_B through a reversible cyclic device. It is also connected to a work consumer (this system is necessary but usually not mentioned) (fig. 1).

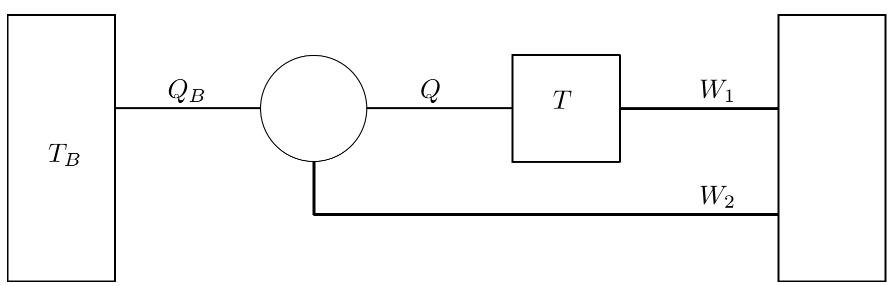

fig.1

If the inequality (1) is violated then

$$\oint \frac{dQ}{T} = \frac{Q_B}{T_B} > 0,$$

where Q_B is the amount of heat received by the reversible device from the energy reservour. Due to the conservation of energy principle all this heat is converted

to the work. But the Kelvin-Plank statement of the second law states that it is impossible to take heat from one system, to give work to another system and to make no changes in any other system. Thus we have a contradiction.

In this proof it is implicitely assumed that we may complete the cycle without making any changes in any system except for the four systems shown in fig.1. However, as we shall see, this assumption may be wrong.

2. The adiabatic process should not be an isentropic one

The *xenium* is a gas whose molecules may be in two different states with the same energy levels. The spontaneous transitions between this states are very rare. However two sufficiently close molecules may exchange their states. It does'n matter whether the xenium exists. The question is whether the existance of a gas with these properties violates some law of nature or not. In author's opinion, it does not.

If in xenium the number of molecules in one of states is more then in another state then we may consider this metastable gas as a mixture of, say, xenium-1 and xenium-2. Let us consider the vessel of xenium-1 and another one of equilibrum xenium at the same temperature. Two vessels are separated by the membrane which is thin and don't prevent molecules from interacting (fig. 2).

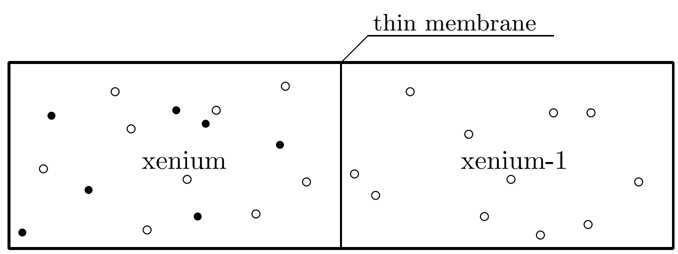

fig.2

Then the equilibrum xenium will be enriched with xenim-1 and entropy of this gas will *decrease* without any heat flow. The only explanation of this paradox is the conclusion: *entropy may be transferred from one system to another system adiabatically.*

Taking into account this process, the inequality (2) should be replaced by

$$dS \geq \frac{dQ}{T} + dI, \tag{4}$$

where dI is entropy absorbed by the system "by the direct way". The inequality (1) takes the form

$$I + \oint \frac{dQ}{T} \leq 0. \tag{5}$$

If $I < 0$ then (1) may be violated.

3. Semiperpetuum mobile

To build a system violating (1) we have to use some extra tricks. The most simple is a selective membrane which is permeable for xenium-1 only (it may be replaced by a substance reacting with xenium-1, this is less convenient but more realistic). This membrane is thick and don't allow molecules to interact through it.

Our perpetuum mobile of the second kind is a cylinder with a piston on one side, closed with a thin membrane on the other side. The cylinder is divided into two parts by a selective membrane. The volume between two membranes is filled by xenium (fig. 3). This device has a straight connection to a heat reservour and works isothermically. Besides, we have two large reservours with xenium-1 one and with xenium-2 another.

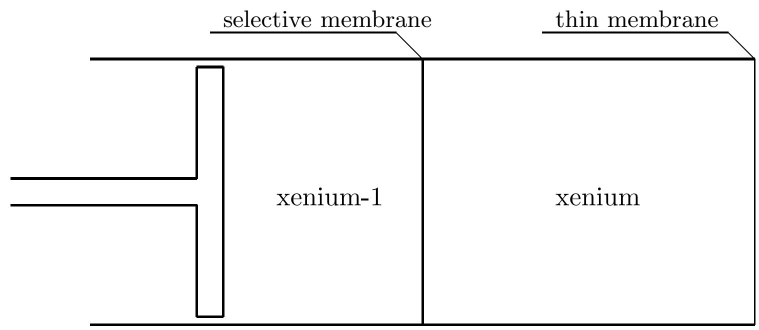

fig.3

At the begining of the cycle the piston is pushed to the selective membrane and the gas is in equilibrum. Then the device is connected to the reservour with xenium-1 for some time, so the gas in the cylinder becames enriched with xenium-1. Then the isothermic expansion follows. After the expansion ends the device is connected to the reservour with xenium-2 until the number of molecules in two states *in all the cylinder* becames equal. The isothermic compression completes the cycle.

Note that the working gas is the xenium-1 only. The expansion takes place at higher (partial) pressure of xenium-1 then the compression. Hence this device produces the work and consumes the heat, violating the inequality (1). However, no contradiction to the second law arises because entropy of reservours increases.

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